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Phenolic Resins

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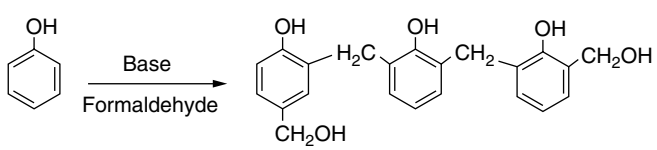
Synthetic phenolic resins were developed and commercialized in the early 1900s by Leo Baekland.[1] The reaction of phenol and formaldehyde produces a product that forms a highly cross-linked three-dimensional polymer when cured. The resins have found use in various applications in the coatings industry because of their excellent heat resistance, chemical resistance, and electrical properties. They also offer good adhesion to many substrates and have good compatibility with other polymers.

Phenolic resins have two basic classifications: resoles and novolaks. Resoles, or heat-reactive resins, are made using an excess of formaldehyde and a base catalyst. The polymer that is produced has reactive methylol groups that form a thermoset structure when heat is applied.

Novolaks are made using an excess of phenol and an acid catalyst. Reaction occurs by the protonation of the formaldehyde,[2] and the intermediate is characterized by methylene linkages rather than methylol groups. These products are not heat reactive, and they require additional cross-linking agents such as hexamethylenetetramine to become thermosetting. These reactions can be thought of as nucleophilic attack of phenoxide ion on the formaldehyde, or electrophilic substitution by protonated formaldehyde on the aromatic ring.[3]

Both polymerization reactions evolve water during cure. This condensation reaction serves to limit film thickness to approximately 3 mils, because the volatiles will cause blistering while curing takes place. Baking temperatures are generally 300 to 400°F with a bake time of 10 to 30 min.

Phenolic resin polymers have been used in the coatings industry for many years because of their excellent performance properties and their relatively low cost. Some of the major applications are in rigid packaging, maintenance primers, printing inks, and epoxy hardeners. A brief discussion of these applications follows.



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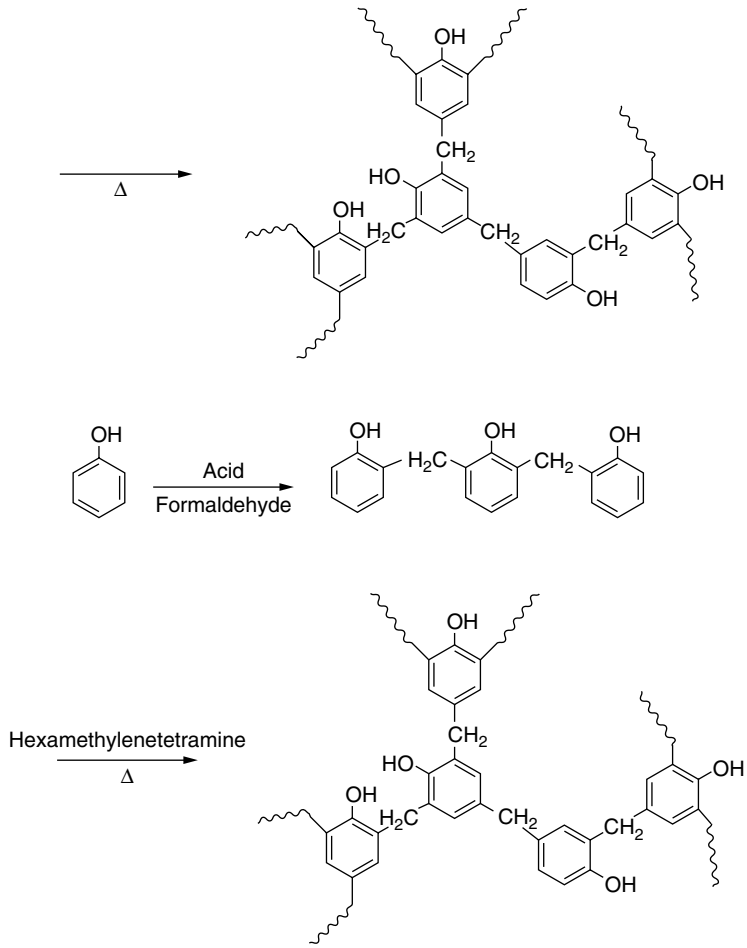

53.1 Rigid Packaging

Phenolic resins have found use in metal containers because they offer outstanding corrosion protection and excellent adhesion, along with chemical and solvent resistance. Typical end-use applications are food container coatings, drum and pail lining, pipe coatings, tank linings, and coil coating primers, or certain polyester resins.

Unmodified phenolics are often used in drum, pail, and pipe coatings. Since the substrate is usually rigid, the brittleness associated with these phenolic formulations does not present a problem. The excellent solvent resistance of phenolic resins makes them ideal for this application. A film thickness of 0.2 to 0.3 mils often provides sufficient protection. Thicker films can also be used if coatings are applied in several layers to prevent blistering during cure.[3] Bake schedules generally range from 300 to 400°F with times varying from 10 min to several hours. The coatings may be clear or pigmented with iron oxide. A typical formulation is listed in Table 53.1. Formulations may be applied by spray, brush, or roller coating.

The requirements of food can linings are quite different from those of drum coatings. Food can coatings must have sufficient flexibility to survive any impact that could fracture the coating and thus expose the metal surface to the contents of the can.[4] The phenolic resins are based on blends of phenol and cresols that offer varying degrees of flexibility and chemical resistance. Resins based on bisphenol A are used in critical taste applications. High molecular weight epoxies are used as modifiers to further enhance the flexibility of the cured films.

Another consideration for food can formulations is sulfur staining. Foods high in protein such as meats and fish contain sulfur, which may permeate to the substrate and cause discoloration.[5] Phenolics,

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TABLE 53.1 Drum and Pail Lining

Ingredients	Parts by Weight
Phenolic resin[a]	73.30
Acetone[b]	7.00
Methyl ethyl ketone	9.00
Ethanol	55.00
Propyl Propasol solvent	14.00
Cyclohexanone	15.00
Leveling agent	0.05

[a] BKS-2600, Union Carbide Corp.
[b] Silwet L-7602, Union carbide Corp.
Source: Union Carbide Corp., Formulation Suggestions — Durable Phenolic Baking Coatings for Rigid Metal Substrates (F-60675), 1988.

TABLE 53.2 Food Container Formulation

Ingredients	Parts by Weight
Phenolic resin[a]	22.90
Epoxy resin[b]	34.00
n-Butanol	11.30
Methyl Propasol acetate	11.30
85% Phosphoric acid	0.25
Leveling agent[c]	1.00

[a] Ucar BKS-7570, Union Carbide Corp.
[b] Epon 1007, Shell Chemical Co.
[c] Silicon resin SR 882M, General Electric.
Source: From Morrison, R. T., and R. N. Boyd, *Organic Chemistry.* 3rd ed. Boston: Allyn and Bacon, 1973, p. 1147.

because of their high degree of cross-linking, offer outstanding resistance to sulfur-containing foods. A food container formulation is listed in Table 53.2.[6]

53.2 Maintenance Primers

Non-heat-reactive phenolics are used in combination with drying oils or alkyds to produce air drying maintenance coatings. The phenolic resins supply solvent and moisture resistance, while the oils or alkyds impart flexibility and good filming characteristics.[7] In the past, parasubstituted phenolic novolak resins were actually cooked with unsaturated oils such as linseed or castor oil.[8] The mixtures were boiled at 400 to 500°F until a thick resinous solution was produced. The reaction mechanism is not completely understood, but it is believed that quinone methylide structures in the phenolic resins react with the double bond in the oil through a Diels-Alder type of reaction.[9] The resin solution is then let down in mineral spirits or aromatic solvents along with metal driers such as cobalt or manganese. Usually a combination of driers gives the best overall performance.[10] The result is an air dry finish that has excellent weathering resistance. Today, it is increasingly popular to simply cold-blend phenolic resins[11] based on *p-tert*-butyl phenol along with solvents, driers, and highly reactive oils such as tung oil. Coating properties are excellent, and the procedure takes less energy and time.

53.3 Printing Inks

Phenolic resins are used in numerous printing ink formulations. Lithographic, letterpress, and gravure inks are oleoresinous and have phenolic resins added to the ink systems to improve film hardness and

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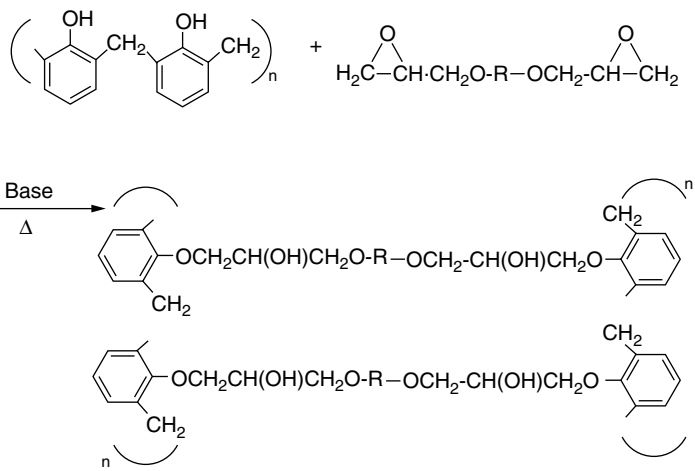
gloss.[12] Parasubstituted phenolic novolak resins that have been modified with rosin make excellent ink additives. Rosin modification of the phenolic resin raises the melting point and gives the phenolic excellent oil solubility. The formulations consist of a phenolic resin, oils, pigments or dyes, driers, and lubricants or plasticizers.[13] The proper balance of ingredients gives the desired combination of hardness, viscosity, penetration, and drying rate.

53.4 Epoxy Hardeners

Phenolic resins may be combined with epoxy resins for use in protective coatings. Phenolic–epoxy products are also used in laminates, prepreg manufacturing, molding materials, and electrical insulation coatings. The phenolic resin is used as a coreactant to produce thermoset systems with improved heat and chemical resistance. Non-heat-reactive (novolak) resins are used to cross-link the epoxies. The epoxy resins are typically epoxy–phenolics or bisphenol A-based resins.[14] The reaction mechanism is different from the resole–epoxy reactions. The coating is heat-activated and uses a base catalyst such as an amine, dicyandiamide, or an imidazole.[15] The phenolic hydroxyl group reacts with the epoxy group to form a polyether structure, which has an advantage, because no volatiles are released during cure. This allows for thick films to be produced with low shrinkage and no voids from volatile emission. The phenolic–epoxy reaction using a base catalyst can be demonstrated as follows:



For critical electrical applications, "high purity" resins are used. These products are made according to stringent specifications limiting the amount of water, ions, and free monomers present in the resin.

53.5 Summary

Phenolic resins were one of the first synthetic polymers to have widespread commercial importance. Their outstanding performance properties have given them a permanent role in the coatings industry. They are used in applications ranging from railroad tank cars to carbonless copy paper. Phenolic resins are also used on a wide variety of substrates including metal, wood, paper, and ceramics. There are so many types of phenolic resin available to the marketplace that a particular resin can be selected for virtually any application.

Phenolic resins should not be overlooked when choosing a high performance polymer. Phenolics currently do not receive the same attention as some of the more recently developed polymers, but for many applications, there is simply no substitute for phenolic resins. Phenolics will continue to have an important role in the coating industry because of their versatility, coatings properties, and reasonable price.

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